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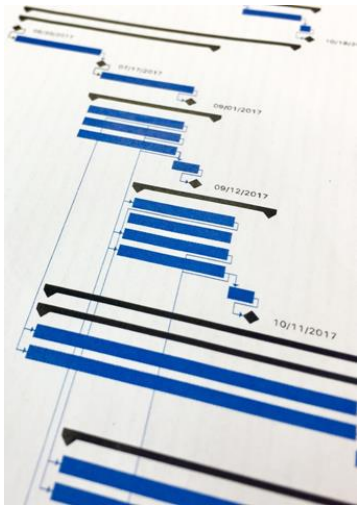
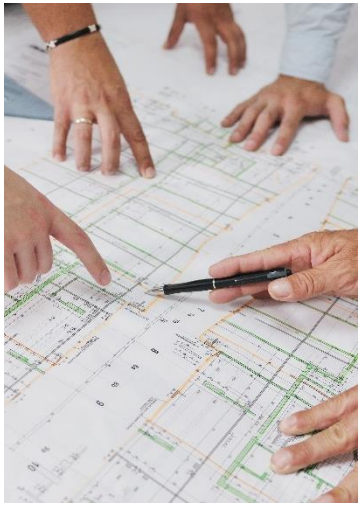
TRUST – PERFORMANCE – PEOPLE

Environmental and Infrastructure Solutions


Progress in Development of Stack Sampling Methods to Measure PFAS in Air Emissions from Stationary Sources

April 2022

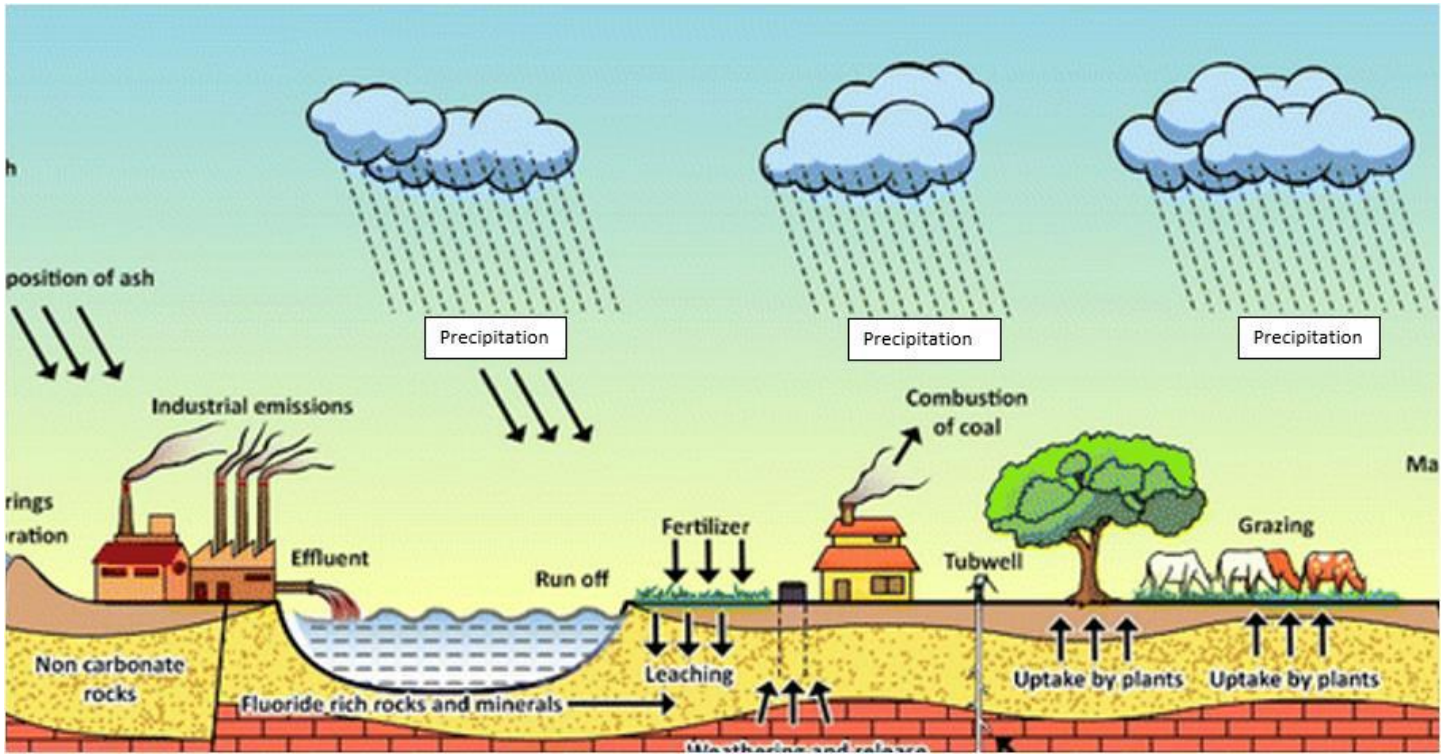
60+ Years of Environmental Excellence

PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

PFAS in Air Source Emissions

- Focus on PFAS has been in Drinking Water, Groundwater, Soil
- Very little focus on Air to date, But that's changing
- Few regulatory standards for PFAS in Air; Permits with DRE or informational testing
- No EPA validated ambient air monitoring methods for PFAS
  - Deposition Sampling
  - Ambient Air Monitoring TO-13A
- EPA Draft Other Test Method 045 (OTM-45) stack testing method for PFAS released in January 2021

Why Air?



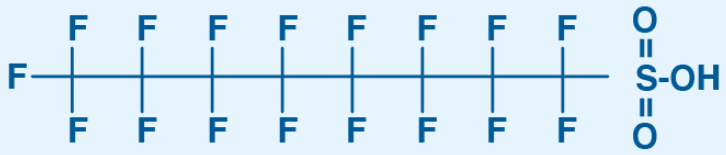
https://www.picswe.com/

What PFAS Are We Looking For?

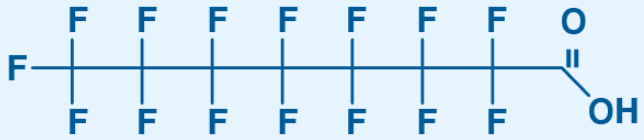
Over 6000+ PFAS Compounds

- EPA Method 537.1 (18 PFAS compounds)
  - Determination of PFAS in drinking water by solid phase extraction (SPE), liquid chromatography/tandem mass spectrometry (LC/MS/MS),
- EPA Method 533 (25 PFAS compounds)
  - Determination of PFAS in drinking water by Isotope dilution anion exchange, SPE, and LC/MS/MS,
- EPA Method 8327 (24 PFAS Compounds)
  - Analysis of surface water, groundwater, and wastewater matrices, LC/MS/MS
- EPA Draft Method 1633 (40 PFAS compounds)
  - Analysis PFAS in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS
- EPA Draft Method OTM-45 (~50 PFAS compounds)
  - Measurement of Selected PFAS from Stationary Sources (Stack Testing)

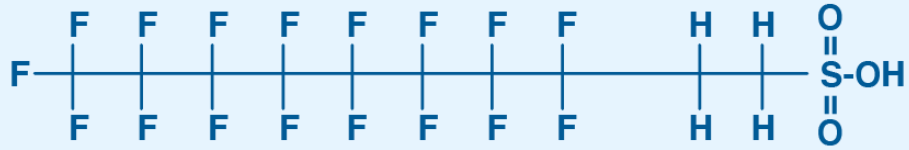
Per vs Poly PFAS



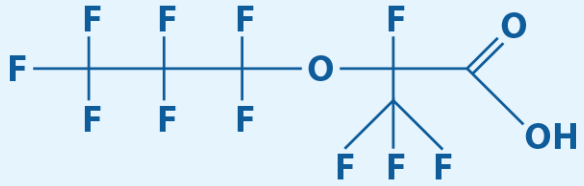
perfluorooctane sulfonic acid
(PFOS, CAS 1763-23-1)



perfluorooctanoic acid
(PFOA, CAS 335-67-1)



8:2 fluorotelomer sulfonate
(8:2 FTS, CAS 039108-34-4)



Hexafluoropropylene oxide-dimer acid
(HFPO-DA, CAS 13252-13-6)

Draft EPA Method OTM-45

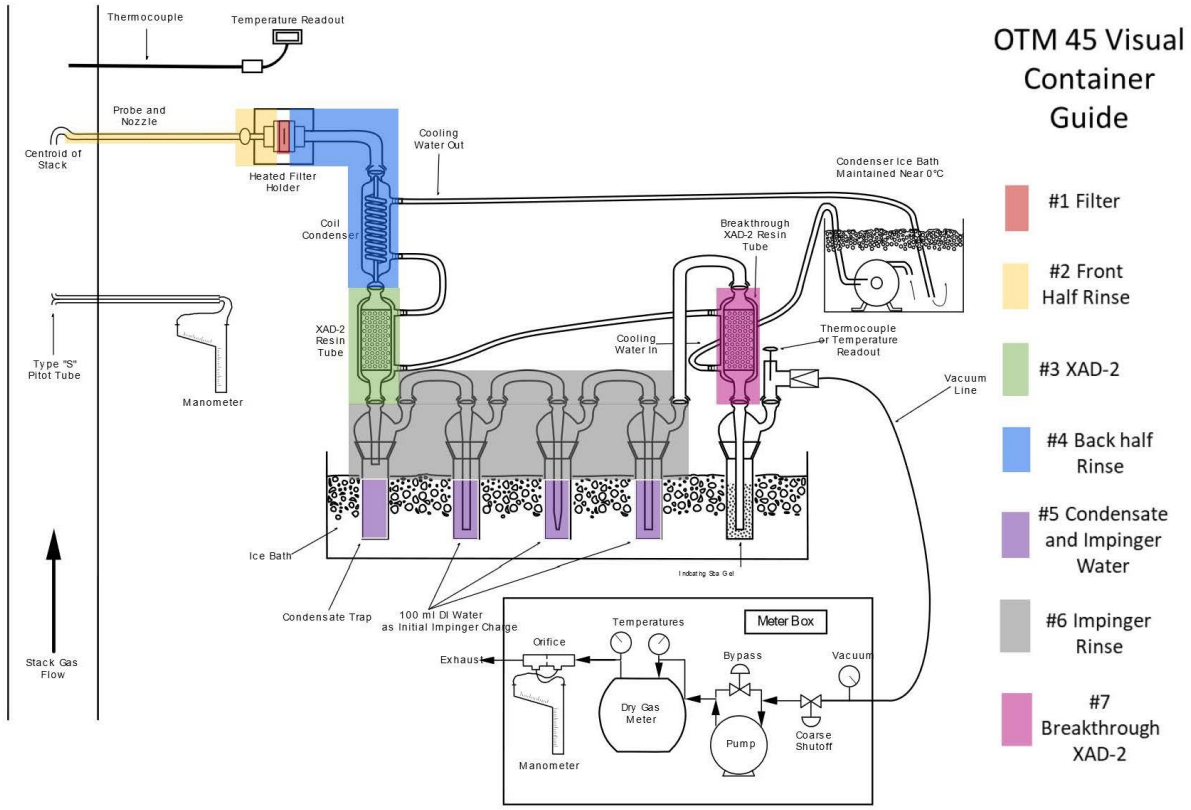
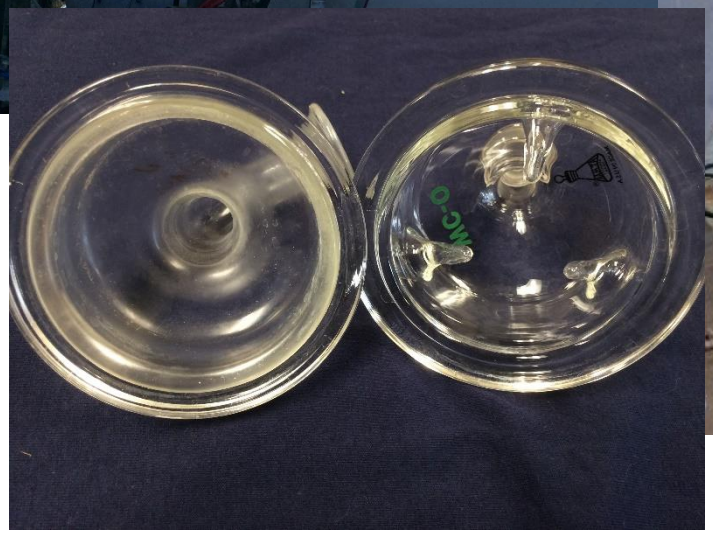


Figure OTM-45-1. Sampling Train

- Isokinetic Sampling Method
- Four Sample Fractions
- Blank train – Proof Blank
- LC/MS/MS Analysis
- Semi-volatile, Polar PFAS
- Isotope Dilution – Isotopically Labeled Standards

Draft EPA Method OTM-45 Isokinetic Train

Draft EPA Method OTM-45 Isokinetic Train



Blank Contamination

- OTM-45 Glassware Cleaning procedure
- Laboratory Prep of XAD Resin
- Clean and Prep Mobile lab
- Revised Sampling Equipment Handling Procedures
- Revised Sample Recovery Procedures
- Limit Access to Mobile Lab
- To PTFE or not to PTFE

Breakthrough

ANALYTICAL FRACTION WORKSHEET

		FH	Q		BHS/ XAD1	Q		BH Condensate	Q		XAD2	Q		Subtotal Fractions 1,2,3	XAD2 Breakthrough Percentage		Total Catch (ng)	Total Catch (ug)
LABORATORY REPORT DATA, ng.																		
Perfluorobutanoic acid (PFBA)		**0.498**			**15.0**			**9.23**			**3.29**			**24.728**	**13.3%**		**28.018**	**0.0280**
N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	**<**	**0.140**		**<**	**0.190**		**<**	**0.0960**		**<**	**0.190**		**<**	**0.426**	**0.0%**	**<**	**0.426**	**0.0004**
2-(N-ethylperfluoro-1-octanesulfonamido) ethanol (N-EtFOSE)		**5.130**		**<**	**1.00**		**<**	**0.237**		**<**	**1.00**		**≤**	**5.130**	**0.0%**	**≤**	**5.130**	**0.0051**
Perfluorohexanoic acid (PFHxA)	**<**	**0.210**			**9.10**	**B,FB**		**2.39**			**0.75**	**B**	**≤**	**11.490**	**6.5%**	**≤**	**11.490**	**0.0115**
Perfluoroheptanoic acid (PFHpA)	**<**	**0.110**			**9.07**	**B,FB**		**0.751**			**2.99**	**B**	**≤**	**9.821**	**30.4%**	**≤**	**12.811**	**0.0128**
N-methylperfluorooctanesulfonamidoaetic acid (NMeFOSAA)	**<**	**0.119**			**0.142**	**J**	**<**	**0.146**			**0.194**	**J**	**≤**	**0.142**	**136.5%**	**≤**	**0.336**	**0.0003**
2-(N-methylperfluoro-1-octanesulfonamido) ethanol (N-MeFOSE)	**<**	**0.280**		**<**	**1.00**	***-,*1**	**<**	**0.131**			**1.52**	**CI,B,*+,*1**	**<**	**1.411**	**107.7%**	**<**	**2.931**	**0.0029**

Notes:

Subtotal of Fractions 1, 2, 3 does not include non-detect values. If all three fractions are non-detects then the subtotal shown is the sum of all three non-detect values.

The Fraction 4 (breakthrough XAD) value is only included in the Total Catch for each fraction if the breakthrough percentage for that fraction is greater than 10%.

Q = Data Qualifier

J = Result is less than the reporting limit but greater than or equal to the method detection limit. The concentration is an approximate value.

B = Compound was found in a lab blank sample

FB = Compound was found in a field blank sample at a level above the reporting limit. Field blanks with "J" values are not flagged here but are shown in the analytical report.

I = The value is an estimated maximum posssible concentration

CI = The peak exhibited chromatographic interference that could not be resolved. The value may be biased high.

*- = LCS or LCSD are outside the acceptance limits, biased low.

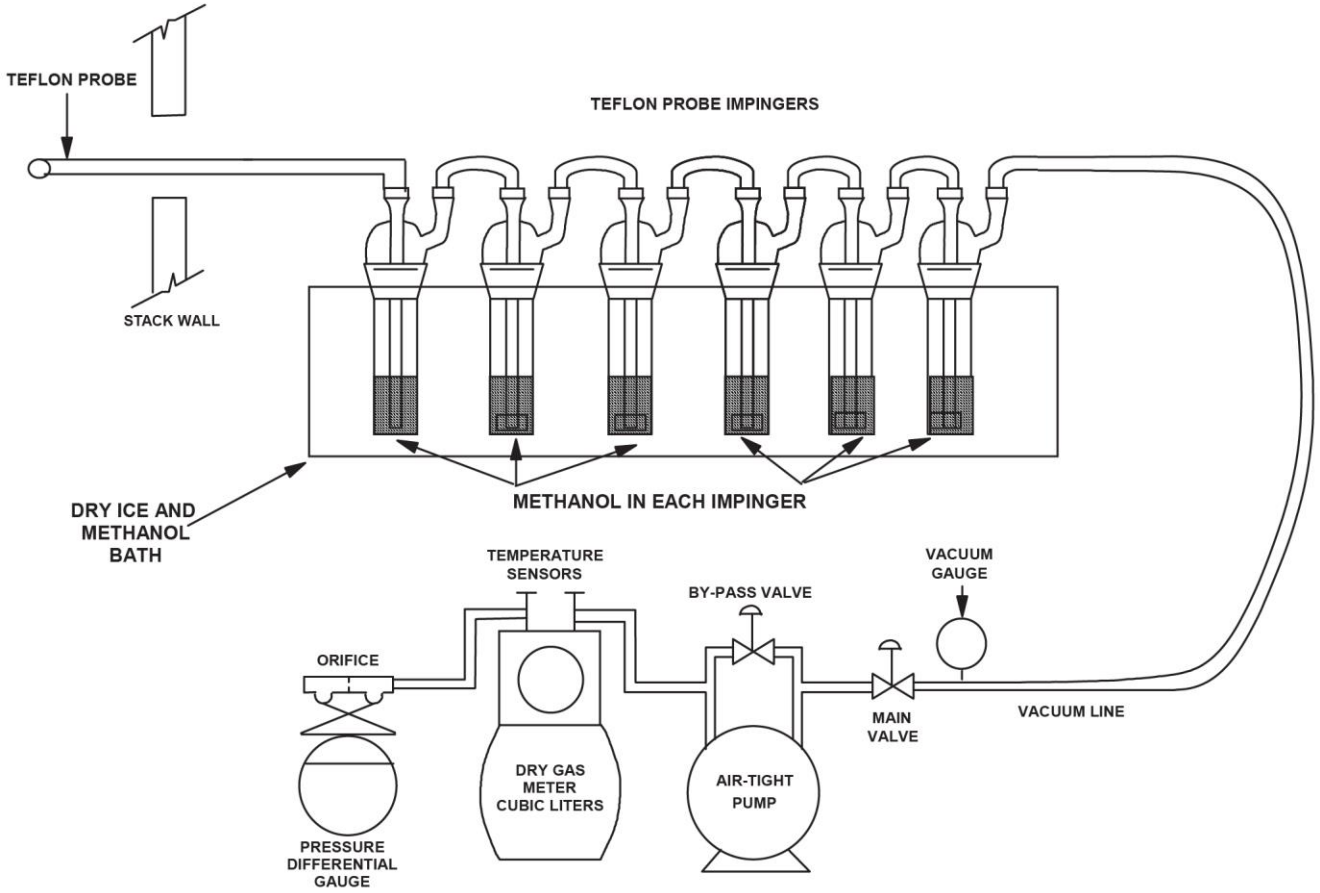
*+ = LCS or LCSD are outside the acceptance limits, biased low.

*1=LCS/LCSD RPD exceeds control limits.

< = Not detected in Fractions 1,2,and 3 at the Method Detection Limit. MDL values are reported.

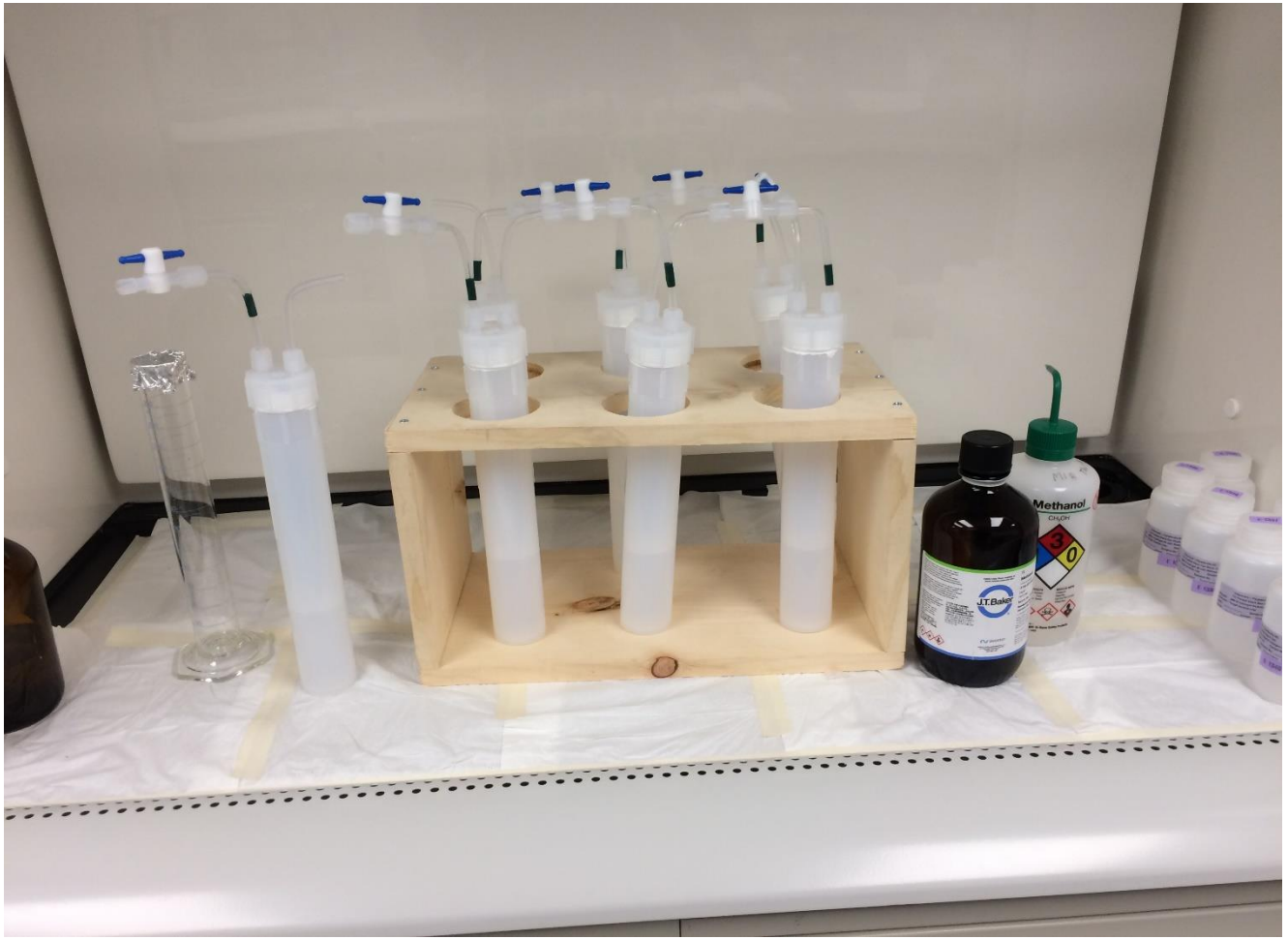
≤ = Subtotal of Fractions 1,2, and 3 is a summation of only the detected values.

Modified EPA Method 18 Cryogenic Train

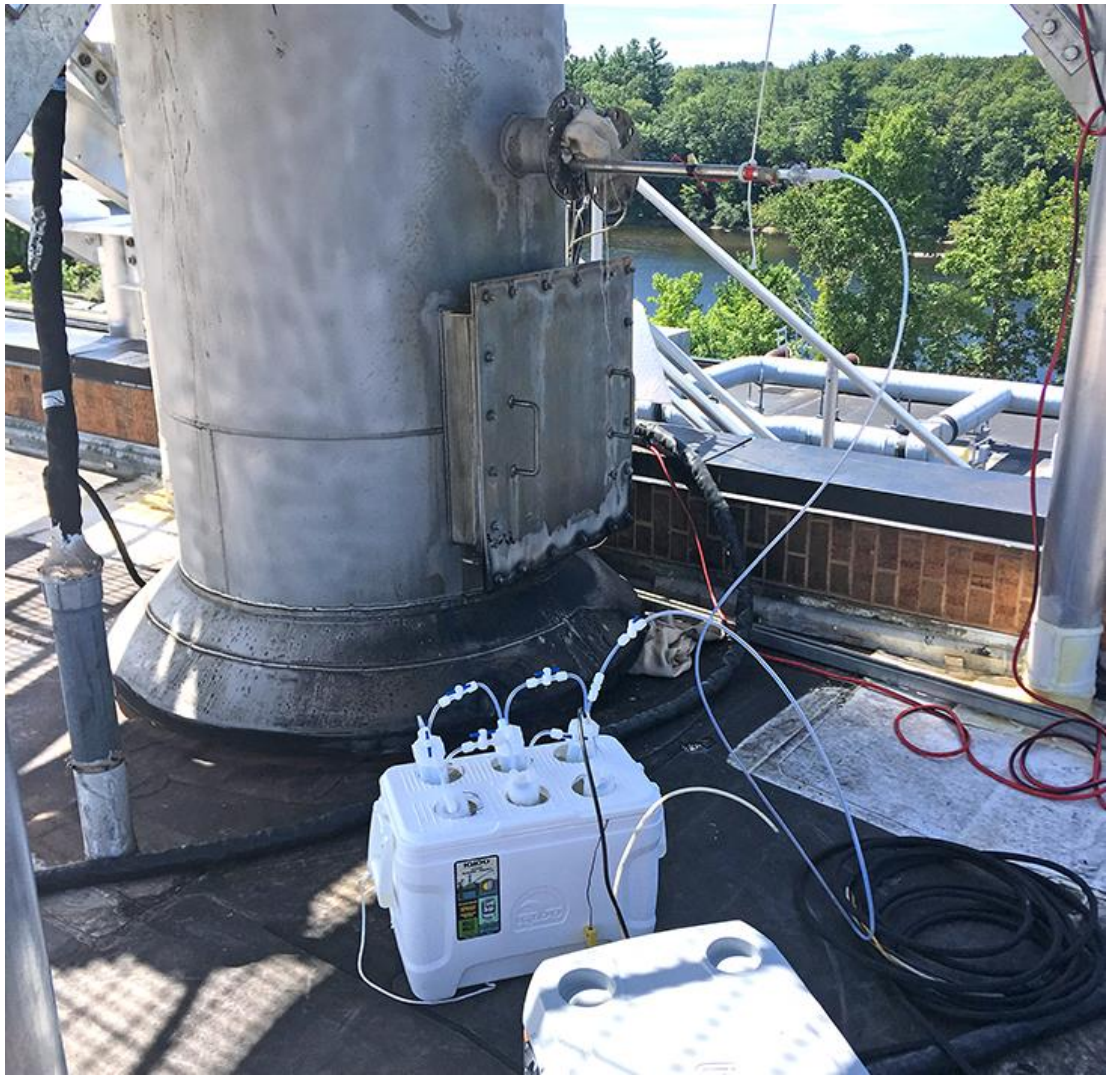


- Non-Isokinetic Sampling Method
- Methanol in Impingers - Separate Sample Fractions
- GC/MS Analysis
- Methanol Bath Chilled to -100 °F

Modified EPA Method 18 Cryogenic Train



Modified EPA Method 18 Cryogenic Train



Detection Levels

- OTM-45 detection limits
  - 0.05ng to 2.8ng/sample
  - Varies per fraction, per compound, per lab
  - equal to ppq in-stack PFAS concentrations (Table 45-11)
- Modified Method 18 detection limits
  - 2.5ng to 50ng/sample
  - equal to ppt in-stack PFAS concentrations

Processes Tested by Weston

- Chemical Manufacturing
- Coating Operations
- Sewage Sludge Incinerator
- Carbon Regeneration

Potential Sources of PFAS Air Emissions

- Chemical Manufacturing
- Coating Operations
- Sewage Sludge Incineration
- AFFF (DOD)
- Refineries
- Pulp and Paper
- Waste Incineration
- Carbon Regeneration
- Landfills
- Others……..

PFAS Air Pollution Control Systems

- Thermal Oxidation
- Scrubbers
- Carbon Beds
- Air Stripper
- Incineration
- Others??

Other PFAS Sampling/Analytical Methods

- EPA Canister Sampling Method
  - Measure Highly volatile PFAS, non-polar
- Total Organofluorine (TOF) Analysis – Combustion IC
  - Measure Total Fluorine – separate HF
  - Subtract HF measured by EPA Method 26 or other methods
- Total Oxidizable Precursors (TOP) Analysis
  - Converts polyfluorinated precursor PFAS compounds to measurable forms of PFAS
- Time-of-Flight – Non-target Analysis
  - Liquid Chromatography Quadrupole Time-of-Flight Spectrometry
  - Not Quantitative - Determines chemical structure to identify compounds
- OTM-45 Sequential Extractions
  - MeOH and separate MeCl extractions for fluorotelomers

Future

- EPA 2019 PFAS Action Plan
  - EPA Administrator Michael Regan is from NC
  - April 27, 2021 – EPA Council on PFAS
- EPA Validation and Promulgation of Stack Testing Methods
- Legal action by state regulatory agencies
- Regulatory agencies will determine industries and processes to be regulated, which PFAS compounds to be measured, and will establish air emission limits
- Lawyers, Engineers, Chemists, and…… Stack Testers

Acknowledgements and Contacts

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Questions?